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(54) **POLYOXYMETHYLENE COMPOSITION AND MOLDED ARTICLE.**

(57) A polyoxymethylene composition comprising (A) 100 parts by weight of polyoxymethylene, (B) 0.01 to 5 parts by weight of a hindered phenol compound, (C) 0.01 to 5 parts by weight of a specified phosphorus compound, and (D) 0.01 to 5 parts by weight of a specified nitrogenous or metallic compound, and having an excellent resistance to an aqueous hypochlorite solution; and a molded part or container made therefrom.

**EP 0 580 872 A1**

Field of the Invention

The present invention relates to a polyoxymethylene composition having an excellent resistance to an aqueous hypochlorite solution, particularly a composition prepared by blending polyoxymethylene with a hindered phenol compound, a specified phosphorus compound and a specified nitrogenous or metallic compound, and a part or container molded from the composition.

Related Art

A polyoxymethylene resin has well-balanced mechanical properties, high heat resistance, fatigue resistance higher than that of any other plastic, excellent friction and wear characteristics and excellent chemical resistance. Thus, a polyoxymethylene resin serves as an excellent engineering plastic; still, the resin is required to have a further improved resistance to chemicals such as an aqueous hypochlorite solution, when applied to some fields. Such a field requiring a further improvement in the chemical resistance includes city water-related parts such as pipe, joint and water meter; mechanical parts of a water boiler, dishwasher or washing machine; and a container, stopper and spray part for various bleaching agents or chlorinated detergents.

Up to this time, polyoxymethylene has been mainly used as the material of the mechanical parts of a water meter or the like. However, the amount of calcium hypochlorite added to city water as a bactericide has recently increased with a lowering in the quality of service water supplied to midtown and industrial areas, so that the inner part of a water meter or the like undergoes blushing and peeling before its guaranteed life expires and the resin peeling off from the surface of the part clogs a pipe to impair the function thereof unfavorably. Accordingly, an improvement in this respect has been expected.

Generally, a hindered phenol antioxidant or a heat stabilizer such as polyamide or a hydroxide or organic or inorganic acid salt of an alkali or alkaline earth metal is added to polyoxymethylene.

However, the above addition is insufficient to solve the above problem. Particularly, a large amount of an additive must be added to enhance the resistance of polyoxymethylene to an aqueous solution of sodium hypochlorite. The addition of a large amount of an additive, however, causes blooming of a stabilizer or the like and brings about significant adhesion thereof to a mold as mold deposit, thus being disadvantageous to mass production. Further, the addition is also costly, so that a further improvement has been expected.

Disclosure of the Invention

The present inventors have extensively studied to obtain a polyoxymethylene composition satisfying the above requirement and have found that the behavior of polyoxymethylene against an aqueous hypochlorite solution can be improved by adding at least three components, i.e., a hindered phenol compound, a specified phosphorus compound and a specified nitrogenous or metallic compound. The present invention has been accomplished on the basis of this finding.

Namely, the present invention relates to a polyoxymethylene composition having an excellent resistance to an aqueous hypochlorite solution, which comprises

(A) 100 parts by weight of polyoxymethylene, and, incorporated therewith,

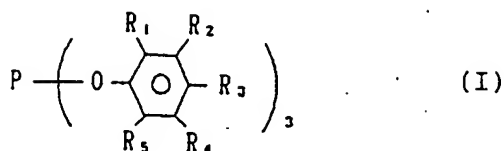
(B) 0.01 to 5 parts by weight of a hindered phenol compound,

(C) 0.01 to 5 parts by weight of a phosphorus compound represented by the general formulae (I) or (II),

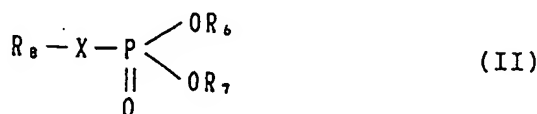
and

(D) 0.01 to 5 parts by weight of at least one compound selected from among nitrogen compounds (D-1) represented by the formulae (III) or (IV), metal oxides (D-2) represented by the formula (V) and metal hydroxides or alkoxides (D-3) represented by the general formula (VI),

and a molded article made therefrom which is used in water-related fields such as water supply:



wherein  $R_1$  to  $R_5$  each represent hydrogen, a saturated or unsaturated, linear or branched alkyl group having 1 to 20 carbon atoms, an alkoxy group, a substituted or unsubstituted phenyl group or a substituted or unsubstituted phenyloxy group,

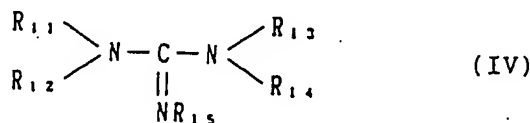


wherein  $R_6$  and  $R_7$  each represent a saturated or unsaturated, linear or branched alkyl group having 1 to 20 carbon atoms;

$R_8$  represents a substituted or unsubstituted phenyl group, a 4-hydroxy-substituted phenyl, a substituted or unsubstituted 4-piperidiny group, a substituted or unsubstituted 3-pyrrolidiny group or hydrogen; and X represents a saturated or unsaturated, linear or branched alkylene group having 1 to 20 carbon atoms which may have an ether or ester bond in the molecular chain thereof or X may be absent,



wherein  $R_9$  and  $R_{10}$  each represent a saturated or unsaturated, linear or branched alkyl group having 1 to 20 carbon atoms,



wherein  $R_{11}$  to  $R_{15}$  each represent a saturated or unsaturated, linear or branched alkyl group having 1 to 20 carbon atoms or a substituted or unsubstituted phenyl group which may have an ether, ester or amide bond or the like in the molecular chain thereof,

$M_1O$  (V)

wherein  $M_1$  represents Mg, Ca, Ba or Zn,

$M_2(OR_{16})_m$  (VI)

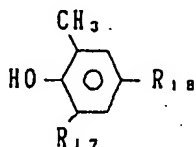
wherein  $M_2$  represents K, Na, Mg, Ca, Ba or Zn;

$R_{16}$  represents an alkyl group having 1 to 18 carbon atoms or hydrogen; and  $m$  represents 1 or 2.

The constitution of the present invention will now be described in detail.

The polyoxymethylene to be used in the present invention as the component (A) is a polymer comprising, as its mainly constituent units oxymethylene groups ( $-\text{CH}_2\text{O}-$ ), which may be either a polyoxymethylene homopolymer or a copolymer, terpolymer or block copolymer containing a small amount of other constituent units in addition to oxymethylene groups. Further, the polyoxymethylene may be either a linear one or a branched or crosslinked one. Furthermore, the degree of polymerization thereof is not particularly limited.

The hindered phenol compound (B) to be used in the present invention includes 2,2-methylenebis-(4-methyl-6-t-butylphenol), 1,6-hexanediol-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], pentaerythritol tetrakis[3-(3,5-di-t-butyl-4-hydroxy-phenyl)propionate], triethylene glycol-bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate], 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, n-octadecyl-3-(4'-hydroxy-3',5'-di-t-butylphenol)propionate, 4,4'-methylenebis-(2,6-di-t-butylphenol), 4,4'-butylidene-bis(6-t-butyl-3-methyl-phenol) 2,2'-thiodiethyl-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], di-stearyl-3,5-di-t-butyl-4-hydroxybenzylphosphonate, 2-t-butyl-6-(3-t-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenyl acrylate, N,N'-hexamethylenebis(3,5-di-t-butyl-4-hydroxy-hydrocinnamamide), 4,4'-methylenebis(2-methyl-6-t-butylphenol), dioctadecyl ester of (3-methyl-4-hydroxy-5-t-butylbenzyl)-malonate, 2,2'-butylidene-bis-(4,6-dimethylphenol), 2,2'-butylidene-4,6-dimethylphenol-4',6'-di-t-butylphenol, 2,2'-butylidene-bis-(4-t-butyl-6-methylphenol), 2,2'-methylene-bis-(4,6-dimethylphenol), 4,4'-methylene-bis-(2,6-dimethylphenol) and 2,2'-dihydroxy-3,3',5,5'-tetramethylstilbene, which may be used either alone or as a mixture of two or more of them. Among these compounds, those represented by the general formula (VII) are preferable.



(VII)

wherein  $R_{17}$  represents a saturated or unsaturated, linear or branched alkyl group having 1 to 20 carbon atoms; and

$R_{18}$  represents a saturated or unsaturated, linear or branched alkyl group having 1 to 20 carbon atoms or a substituted or unsubstituted phenyl group which may have an ether, ester or amide bond in the molecular chain thereof.

Specific examples thereof include triethylene glycol-bis-[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)-propionate], 4,4'-methylenebis-(2-methyl-6-t-butylphenol), dioctadecyl ester of (3-methyl-4-hydroxy-5-t-butylbenzyl)-malonate and 2,2'-butylidene-bis-(4-t-butyl-6-methylphenol).

According to the present invention, the amount of the hindered phenol compound (B) to be added is 0.01 to 5 parts by weight, preferably 0.3 to 4 parts by weight, still preferably 0.7 to 2 parts by weight based on 100 parts by weight of polyoxymethylene. When the amount is less than 0.01 part by weight, the resulting molded article will suffer from serious peeling and blushing, thus being unfit for practical use, while when it exceeds 5 parts by weight, the resulting molded article will suffer from serious yellowing unfavorably.

Further, the phosphorus compound (C) to be used in the present invention is, as described above, one represented by the general formulae (I) or (II).

Specific examples of the compound represented by the general formula (I) include triphenyl phosphite, trisnonylphenyl phosphite, tris(2,4-di-t-butylphenyl) phosphite, tris(2-t-butyl-4-methylphenyl) phosphite, tris-(2,4-di-t-amylphenyl) phosphite, tris(2-t-butyl phenyl) phosphite, tris(2-phenylphenyl) phosphite, tris(2-(1,1-dimethylpropyl)-phenyl) phosphite, tris(2,4-(1,1-dimethylpropyl)-phenyl) phosphite, tris(2-cyclohexylphenyl) phosphite and tris(2-t-butyl-4-phenylphenyl) phosphite.

On the other hand, specific examples of the compound represented by the general formula (II) include diethyl ester of 3,5-di-t-butyl-4-hydroxy-benzylphosphonate, dimethyl ester of bis-(hydroxy-4-phenyl)-1,1-ethylphosphonate, dimethyl ester of bis-(hydroxy-4-phenyl)-2,2-propyl-phosphonate, dimethyl ester of bis-(hydroxy-4-phenyl)-3,3-butyl-phosphonate, diethyl ester of bis-(hydroxy-4-phenyl)-2,2-propyl-phosphonate and dimethyl ester of bis-(4-hydroxy-3,5-di-t-butylphenyl)-2,2-octadecyl-phosphonate, which may be used either alone or as a mixture of two or more of them. Among these compounds, tris(2,4-di-t-butylphenyl)

phosphite and diethyl ester of 3,5-di-*t*-butyl-4-hydroxy-benzyl-phosphonate are particularly preferably ones.

According to the present invention, the amount of the phosphorus compound (C) to be added is 0.01 to 5 parts by weight, preferably 0.3 to 2 parts by weight based on 100 parts by weight of polyoxymethylene. When the amount is less than 0.01 part by weight, the resulting composition will suffer from severe discoloration unfavorably, while when it exceeds 5 parts by weight, the resulting molded article will suffer from heavy blooming, thus being unfit for practical use.

The present invention is characterized by adding a specified component (D) represented by one of the general formulae (III) to (VI) in addition to the above-mentioned hindered phenol compound (B) and phosphorus compound (C) to polyoxymethylene (A), and by employing such a constitution, the present invention makes it possible to provide a composition forming a molded article which little suffers from blistering or peeling on the surface of the molded article or formation of white spots due to partial deterioration, and is suppressed in deterioration of appearance due to deterioration as a whole, for example, blushing or yellowing, in an aqueous hypochlorite solution, thus being suitable for the production of mechanical parts of city water-related appliances.

The nitrogen compound (D-1) which is one of the components (D) used for the above purpose is, as described above, one represented by the general formulae (III) or (IV).

Specific examples of the compound represented by the general formula (III) include dimethylcyanamide and diallylcyanamide.

Specific examples of the compound represented by the general formula (IV) include *n*-dodecylguanidine, 1,6-diguanidinohexane, tetramethylguanidine, creatinine aminoguanidine, 1-amino-3-salicyloylguanidine, cyanoguanidine, cyanoguanidine-formaldehyde condensate, *n*-butyldicyandiamide, *n*-pentyldicyandiamide, *p*-chlorophenyldicyandiamide, guanethidine, and *N*-amidino-3-amino-6-chloropyrazinecarboxamide, which may be used either alone or a mixture of two or more of them. Among these compounds, cyanoguanidine, aminoguanidine and dimethylcyanamide are particularly preferably ones.

Further, specific examples of the metal oxide (D-2) represented by the general formula (V) include magnesium oxide, calcium oxide, zinc oxide and barium oxide.

Furthermore, specific examples of the metal hydroxide or alkoxide (D-3) represented by the general formula (VI) include sodium methoxide, magnesium ethoxide, sodium hydroxide, potassium hydroxide, potassium methoxide and barium ethoxide.

The compound (D) to be used in the present invention is preferably one exhibiting a strong basicity, for example, one exhibiting a pH of 10 or above in a state of a 1 vol % aqueous solution.

According to the present invention, the amount of the component (D) to be added is 0.01 to 5 parts by weight, preferably 0.05 to 3 parts by weight, still preferably 0.08 to 1 part by weight based on 100 parts by weight of polyoxymethylene. The addition of the component (D) in an amount less than 0.01 part by weight will be effective a little in activating the hindered phenol, so that the molded article will be unfit for practical use because of severe blushing and peeling, while the addition thereof in an amount exceeding 5 parts by weight will give a molded article suffering from intense yellowing unfavorably.

The composition of the present invention may further contain a conventional reinforcement, extender, lubricant, antistatic agent, colorant, carbon black or the like to impart desired characteristics thereto depending upon the object. The reinforcement includes glass fiber, potassium titanate fiber, calcium carbonate fiber, carbon fiber, talc, mica, glass beads, glass flake and so on. The extender includes calcium carbonate, wollastonite, mineral fibers and so on.

The process for preparing the composition of the present invention is not particularly restricted, and the composition can be easily prepared with conventional equipment for the preparation of resin compositions by a conventional process therefor. For example, the composition can be prepared by any of processes: (i) a process which comprises mixing necessary components together, kneading and extruding the obtained mixture into pellets on an extruder and molding the pellets, (ii) a process which comprises preparing pellets different from each other in their compositions, mixing the pellets at a given ratio and molding the obtained pellet mixture to obtain a molded article having an objective composition, or (iii) a process characterized by feeding one or more of the components directly into a molding machine. Further, a process which comprises preliminarily pulverizing a part of the resin components and mixing the obtained powder with the rest of the components is effective in homogeneous blending of the components.

The polyoxymethylene composition thus prepared is remarkably improved in resistance to an aqueous hypochlorite solution without impairing the mechanical properties, heat resistance and wear and friction characteristics inherent in polyoxymethylene, thereby serving as an excellent chemical-resistant composition. Therefore, the composition is suitable for the production of a mechanical part or vessel of a city water-related appliance such as a water boiler, dishwasher, water meter or washing machine; or a container, stopper or spray part for various bleaching agents or chlorinated detergents.

The resin composition according to the present invention can be molded by any process selected from among extrusion, injection, compression molding, vacuum forming, blow molding and expansion molding.

The polyoxymethylene composition of the present invention and a molded article made therefrom less suffer from peeling or blushing and exhibit a lowered degree of discoloration when used in an aqueous hypochlorite solution, as compared with those of the prior art. Further, the composition of the present invention does not undergo blowing in the residence, so that it is suitable for the production of a container, stopper or spray part for various bleaching agents or chlorinated detergents, or a mechanical part or vessel of a city water-related appliance such as a water boiler, dishwasher, water meter or washing machine.

## 10 Examples

The present invention will now be described more specifically by referring to the following Examples and Comparative Examples. The methods employed in the Examples and Comparative Examples for evaluating the characteristics are as follows.

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### 1) Residence test

Each resin composition was made to remain in an injection machine of a clamping pressure of 75 ton at a cylinder temperature of 200 °C for one hour and thereafter injected through a nozzle to evaluate the extent of blowing with the naked eye.

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evaluation criteria:

- no blowing
- △ a little blowing
- X severe blowing

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### 2) Immersion test against aqueous solution of sodium hypochlorite (appearance change, discoloration resistance)

An ASTM type I test piece for tensile test made from each composition was immersed in a 0.3 vol % aqueous solution of sodium hypochlorite placed in a pressure test tube made of glass having an inner diameter of 45 mm and fitted with a condenser and the solution was refluxed at 80 °C. Samples were taken out at given intervals and evaluated for blistering and peeling of surface, white spot and blushing with the naked eye.

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evaluation criteria:

- scarcely any blister or white spot
- △ several blisters and white spots
- X many blisters and white spots
- XX peeled and blushed

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After the test piece had been subjected to the above treatment for 300 hours, it was examined for degree ( $\Delta E$ ) of discoloration.

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That is, the L, a and b values of the Hunter color specification system of the test piece were determined with a digital colormeter (mfd. by Nippon Denshoku Kogyo (K.K.), Z-300A type) to calculate the degree ( $\Delta E$ ) of discoloration according to the following formula. A smaller  $\Delta E$  value means a higher discoloration resistance.

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$$\Delta E = \sqrt{(L-L_0)^2 + (a-a_0)^2 + (b-b_0)^2}$$

$L_0, a_0, b_0$ : initial values

50

$L, a, b$ : values after the test at 80 °C for 300 hours

Examples 1 to 11 and Comparative Examples 1 to 11

An oxymethylene copolymer was blended with various compounds (i.e., components B, C and D) at a ratio specified in Table I and the obtained blend was continuously fed into a vented twin-screw extruder (30 mm $\phi$ ) and kneaded and extruded at 200 °C to give pellets. The pellets were dried in a circulating hot air oven at 130 °C for 3 hours.

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The resulting pellets were injection molded into a test piece and the above characteristics were evaluated. For comparison, blends characterized by not containing one of the components (B), (C) and (D) and those characterized by containing a phosphorus compound (C') or melamine (D') which is outside the scope of the present invention were also prepared and evaluated. The results are given in Tables 1 and 2.

Table 1

		Example No.										
		1	2	3	4	5	6	7	8	9	10	11
(A) polyoxymethylene	kind	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>1</sub>	A <sub>1</sub>
	pt. wt.	100	100	100	100	100	100	100	100	100	100	100
(B) hindered phenol compd.	kind	B <sub>1</sub>	B <sub>1</sub>	B <sub>1</sub>	B <sub>1</sub>	B <sub>1</sub>	B <sub>1</sub>	B <sub>2</sub>	B <sub>4</sub>	B <sub>1</sub>	B <sub>1</sub>	B <sub>1</sub>
	pt. wt.	0.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
(C) phosphorus compd.	kind	C <sub>1</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub>	C <sub>2</sub>	C <sub>2</sub>	C <sub>2</sub>	C <sub>2</sub>	C <sub>2</sub>	C <sub>2</sub>
	pt. wt.	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
(D) nitrogenous or metallic compd.	kind	D <sub>1</sub>	D <sub>1</sub>	D <sub>2</sub>	D <sub>1</sub>	D <sub>2</sub>	D <sub>2</sub>	D <sub>2</sub>	D <sub>2</sub>	D <sub>2</sub>	D <sub>1</sub>	D <sub>1</sub>
	pt. wt.	0.1	0.1	0.1	0.1	0.1	0.3	0.1	0.1	0.1	0.1	0.1
Residence test		0	0	0	0	0	0	0	0	0	0	0
Resistance to NaOCl	100 hr	0	0	0	0	0	0	0	0	0	0	0
	200 hr	0	0	0	0	0	0	0	0	0	0	0
	300 hr	4	0	0	0	0	0	0	0	0	0	0
	degree of discoloration (300 hr)	0.8	1.0	1.1	1.0	1.1	1.2	5.5	10.2	1.1	1.0	1.2

Table 2

		Comp. Example No.										
		1	2	3	4	5	6	7	8	9	10	11
(A) polyoxymethylene	kind	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>	A <sub>2</sub>
	pt. wt.	100	100	100	100	100	100	100	100	100	100	100
(B) hindered phenol compd.	kind		B <sub>1</sub>	B <sub>1</sub>	B <sub>1</sub>	B <sub>1</sub>	B <sub>1</sub>	B <sub>1</sub>	B <sub>1</sub>	B <sub>2</sub>	B <sub>1</sub>	B <sub>1</sub>
	pt. wt.		0.5	0.5	0.5	0.5	0.5	1.0	1.0	1.0	1.0	1.0
(C) phosphorus compd.	kind	C <sub>1</sub>		C <sub>1</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>1</sub>
	pt. wt.	0.5		0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
(D) nitrogenous or metallic compd.	kind	D <sub>1</sub>	D <sub>1</sub>		D <sub>1</sub>	D <sub>1</sub>	D <sub>1</sub>			D <sub>1</sub>	D <sub>1</sub>	
	pt. wt.	0.1	0.1		0.1	0.1	0.1			0.1	0.1	
Resistance test		o	o	o	x	x	o	o	o	x	x	o
Resistance to NaOCl	100 hr	xx	o	x	o	o	x	x	o	o	o	x
	200 hr	-	x	-	x	x	-	x	x	o	o	x
	300 hr	-	x	-	x	x	-	-	-	x	x	-
	degree of discoloration (300 hr)	-	2.5	-	0.9	1.0	-	-	-	6.0	10.8	-

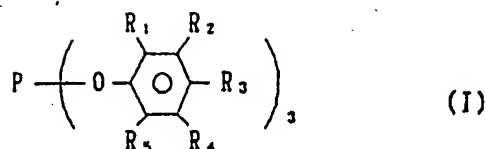


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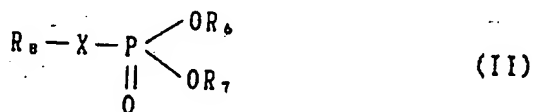
- 5           A<sub>1</sub>: polyoxymethylene copolymer MI=9.0 g/10 min
- A<sub>2</sub>: polyoxymethylene copolymer MI=27.0 g/10 min
- 10          B<sub>1</sub>: triethylene glycol-bis-[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate]
- B<sub>2</sub>: 1,6-hexanediol-bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]
- 15          B<sub>3</sub>: pentaerythrityl-tetrakis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]
- 20          C<sub>1</sub>: diethyl ester of 3,5-di-t-butyl-4-hydroxybenzylphosphonate
- C<sub>2</sub>: tris-(2,4-di-t-butylphenyl) phosphite
- 25          C<sub>1</sub>': tridecyl phosphite
- C<sub>2</sub>': 3,9-distearoxy-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane
- 30          D<sub>1</sub>: aminoguanidine
- D<sub>2</sub>: cyanoguanidine
- 35          D<sub>3</sub>: magnesium oxide
- D<sub>4</sub>: magnesium ethoxide
- 40          D<sub>1</sub>': melamine

#### Claims

- 45 1. A polyoxymethylene composition having an excellent resistance to an aqueous hypochlorite solution, which comprises:
- (A) 100 parts by weight of polyoxymethylene, and, incorporated therewith,
- (B) 0.01 to 5 parts by weight of a hindered phenol compound,
- 50          (C) 0.01 to 5 parts by weight of a phosphorus compound represented by the following general formulae (I) or (II), and
- (D) 0.01 to 5 parts by weight of at least one compound selected from among nitrogen compounds (D-1) represented by the following general formulae (III) or (IV), metal oxides (D-2) represented by the following general formula (V) and metal hydroxides or alkoxides (D-3) represented by the following general formula (VI):
- 55



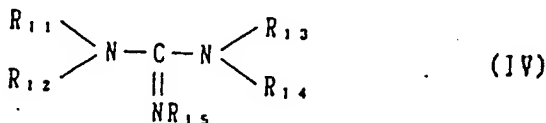
wherein  $R_1$  to  $R_5$  each represent hydrogen, a saturated or unsaturated, linear or branched alkyl group having 1 to 20 carbon atoms, an alkoxy group, a substituted or unsubstituted phenyl group or a substituted or unsubstituted phenyloxy group,



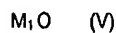
wherein  $R_6$  and  $R_7$  each represent a saturated or unsaturated, linear or branched alkyl group having 1 to 20 carbon atoms,  $R_8$  represents a substituted or unsubstituted phenyl group, a 4-hydroxy-substituted phenyl, a substituted or unsubstituted 4-piperidinyl group, a substituted or unsubstituted 3-pyrrolidinyl group or hydrogen, and  $X$  represents a saturated or unsaturated, linear or branched alkylene group having 1 to 20 carbon atoms which may have an ether or ester bond in the molecular chain thereof or  $X$  may be absent,



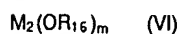
wherein  $R_9$  to  $R_{10}$  each represent a saturated or unsaturated, linear or branched alkyl group having 1 to 20 carbon atoms,



wherein  $R_{11}$  to  $R_{15}$  each represent a saturated or unsaturated, linear or branched alkyl group having 1 to 20 carbon atoms or a substituted or unsubstituted phenyl group which may have an ether, ester or amide bond or the like in the molecular chain thereof,



wherein  $M_1$  represents Mg, Ca, Ba or Zn, and



wherein  $M_2$  represents K, Na, Mg, Ca, Ba or Zn,  $R_{16}$  represents an alkyl group having 1 to 18 carbon atoms or hydrogen, and  $m$  represents 1 or 2.

2. A composition according to Claim 1, wherein the hindered phenol compound (B) is represented by the following general formula (VII):



wherein R<sub>17</sub> represents a saturated or unsaturated, linear or branched alkyl group having 1 to 20 carbon atoms, and

R<sub>18</sub> represents a saturated or unsaturated, linear or branched alkyl group having 1 to 20 carbon atoms or a substituted or unsubstituted phenyl group which may have an ether, ester or amide bond in the molecular chain thereof.

- 15
3. A composition according to Claim 1, wherein the phosphorus compound (C) is tris-(2,4-di-t-butyl-phenyl) phosphite or diethyl ester of 3,5-di-t-butyl-4-hydroxy-benzylphosphonate.
- 20
4. A composition according to Claim 1, wherein the nitrogen compound (D-1) is cyanoguanidine, aminoguanidine or dimethylcyanamide.
- 25
5. A molded part or vessel having an excellent resistance to an aqueous solution containing sodium hypochlorite which is made by molding the polyoxymethylene composition according to Claim 1.
- 30
6. A molding according to Claim 5, which serves as a container, stopper or spray part for bleaching agents or chlorinated detergents, or a mechanical part or vessel of a water boiler, dishwasher, water meter or washing machine.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP93/00180

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl<sup>5</sup> C08L59/00, C08K5/13, C08K5/51, C08K5/32,  
C08K5/17, C08K3/22, C08K5/05

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl<sup>5</sup> C08L59/00-59/04, C08K3/00-5/59

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, A, 1-275652 (Toray Industries, Inc.), November 6, 1989 (06. 11. 89), (Family: none)	1-6
A	JP, A, 52-119652 (CH. CIBA-Geigy AG.), October 7, 1977 (07. 10. 77), & US, A, 4,360,617 & GB, A, 1,560,863 & DE, A1, 2,702,661 & FR, A1, 2,340,343	1-6
A	JP, A, 54-13551 (Asahi Chemical Industry Co., Ltd.), February 1, 1979 (01. 02. 79), (Family: none)	1-6

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

## \* Special categories of cited documents:

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

May 6, 1993 (06. 05. 93)

Date of mailing of the international search report

May 25, 1993 (25. 05. 93)

Name and mailing address of the ISA/

Japanese Patent Office

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